

considerable amounts of sulfite or other silver halide solvent, or it may be based on the silver-solvent developing action of *p*-phenylenediamine. Some of the silver halide crystal is dissolved before chemical reduction is completed. *p*-Phenylenediamine is often used in combination with other developing agents, especially Glycin, to help overcome some of the loss of emulsion sensitivity given by the solvent developing agent that forms image silver of fine particle size but low light-stopping power.

METOL-HYDROQUINONE FINE-GRAIN DEVELOPERS

The Elon-hydroquinone-borax developer known as Kodak developer D-76 was devised by J. G. Capstaff^{4,5} in 1926. This formulation produced maximum shadow detail with a low-contrast image. Today, this solution is often the standard against which other formulations are rated. The formulation of this developer has been widely adopted by others: Ilford ID-11 is identical, and Gevaert G-206 contains one less gram of hydroquinone. Adox MQ and Ansco 17 represent variations of the basic formulation. Developer D-76b is a softer-working version of D-76.

H. C. Carlton and J. I. Crabtree⁶ have found that "The results for any time of development show that with the regular borax developer (D-76) the rate of development increased with keeping. The gamma for 12 minutes development increased from 0.78 to 1.19 in 49 days. With the buffered developer (D-76d) the rate of development remained constant within the limit of error for the 49 days of keeping. For sensitometric purposes which depend upon the development factors remaining constant over a period of several weeks, the buffered borax developer is preferable to the regular formula." (See Table 2 for the formula of Developer D-76 and others.)

D-76 developer has been proposed for one-time use only, then to be discarded. This procedure avoids the possible change in activity of the used developer upon standing. Such a technique may be uneconomical for some if the developer is purchased in less than one-gallon quantities, but the mix-your-own cost involves only a few cents for each roll of film. Dilution of one part of the full strength D-76 developing solution with one part of water provides an economical one-use working solution. Dilution of D-76 with an equal volume of water is now a widespread modern photographic practice, requiring about a 40% increase in the developing time over that required for the undiluted developer. The diluted developer has a contrast-flattening or compensating effect that is particularly useful for processing negatives taken under contrasty lighting conditions.^{7,8} Richard W. Vesey⁹ has suggested that the original processing time for the undiluted developer can be maintained if the 1:1 solution of the developer is six degrees warmer than the temperature for the undiluted developer. A table of processing times for

Table 1. D-76 Processing Times^a with Popular 35mm Films

| Film | Index | Time |
|-------------------|------------|-------------------|
| Adox KB-14 | 32 | 7 min (1:1 dil.) |
| KB-17 | 64 | 8 min (1:1 dil.) |
| KB-21 | 200 | 9 min (1:1 dil.) |
| Agfa Isopan FF | 32 | 7 min (1:1 dil.) |
| F | 40 | 7 min (1:1 dil.) |
| SS | 125 | 10 min (1:1 dil.) |
| Ultra | 400 to 650 | 10 min (straight) |
| Record | 1600 | 13 min (straight) |
| GAF Versapan | 125 | 5½ min (straight) |
| Hypan | 500 | 12 min (1:1 dil.) |
| Hypan | 500 | 7 min (straight) |
| Ilford Pan F | 32 | 7 min (1:1 dil.) |
| FP3 | 125 | 9 min (1:1 dil.) |
| HP3 | 400 | 12 min (1:1 dil.) |
| HPS | 800 | 12 min (straight) |
| Kodak Panatomic-X | 50 | 7 min (1:1 dil.) |
| Panatomic-X | 50 | 4½ min (straight) |
| Kodak Plus-X Pan | 125 | 7 min (1:1 dil.) |
| Plus-X Pan | 125 | 4½ min (straight) |
| Kodak Tri-X Pan | 650 | 11 min (1:1 dil.) |

^a Processing times given here are for 68°F with continuous agitation for the first 30 sec and 5 sec each minute thereafter.

various types of 35mm film, compiled by Vesey, is reproduced here (Table 1), as it shows processing times for the 1:1 dilution of D-76.

Michael Edelson,¹⁰ as well as Vesey, has observed that undiluted D-76 is equally effective over a range of processing temperatures. Edelson has written that

If, for example, the basic time is nine minutes at 68°F, the range would be as follows:

| | | | |
|------|------------|------|------------|
| 69°F | 8¾ minutes | 78°F | 5¼ minutes |
| 70°F | 8¼ minutes | 80°F | 4¾ minutes |
| 72°F | 7½ minutes | 82°F | 4 minutes |
| 75°F | 6½ minutes | 85°F | 3 minutes |

These figures . . . are to be used with agitation for the first 30 seconds of development and for five seconds every 30 seconds thereafter.

Capstaff
1926

Control of the degree of agitation is essential, as the D-76 developing solution has been reported to be particularly affected by it. For example, Vesey noted that

The contrast of any film can be increased or decreased the equivalent of one grade of printing paper by altering the agitation rate as follows:

To Increase Contrast: Agitate the film continuously for the first minute and then at 30-second intervals for the remainder of the processing time.

To Decrease Contrast: Agitate the film continuously for the first 15 seconds of processing and then for two or three seconds every minute of the remaining time.

Normal agitation was continuous for the first 30 sec and for five seconds of each minute of the remaining time.

The Elon-hydroquinone-borax composition of D-76 increases in alkalinity with aeration with keeping or after some use. This results in increased development, so that results are often inconsistent. Even the normal aeration of mixing will make it difficult to achieve exactly the same results from two solutions of this developer, an unfortunate property for a standard developer. This lack of buffering may be overcome by adding four times the normal borax and 8 g of boric acid to the D-76 formulation. This developer, D-76d, gives essentially the same graininess as D-76 at the same developing times.

The introduction of D-76 developer (known as the Eastman borax developer at that time) caused photographic investigators everywhere to study the nature of its fine-grain properties. A summary of some of this early work was given by H. C. Carlton and J. I. Crabtree.⁶

Its ability to produce fine-grained images is undoubtedly a result of the presence of a high content of sodium sulfite which exerts a solvent action on the silver halide grains reducing their size and preventing clumping.¹¹ Namias¹² concludes that the rate of development is too low for practical purposes and claims that his recommended developer . . . [five grams of Metol, fifty grams of sodium sulfite, and five grams of sodium carbonate in a liter of water with 5 ml of phenosafranine (1:1000) present] . . . gives equally fine-grained images with an increase in the rate of development. Lumière and Seyewetz¹³ found that the images produced by borax developer are finer grained than those produced by the same developing constituents used with carbonate as the alkali. Veldman¹⁴ concluded that the borax developer gave very fine-grained images but no finer than the following developer: Elon 15 grams; sodium sulfite (anhydrous) 150 grams; potassium bromide 2 grams, water to 1 liter. This developer is impractical because of the loss in emulsion speed caused by the high bromide content. He varied the sulfite content from 0.5 to 320 grams per liter and found that the graininess decreased as the sulfite content increased. Luppó-Cramer¹⁵ found with the Eastman borax developer that fine-grained images were not obtained with all silver bromide emulsions. Emmermann¹⁶ in a series of tests on motion picture film found that the Eastman borax developer was the best formula known for producing fine-grained images. Nauck¹⁷ concludes that the low alkalinity of the borax developer contributes indirectly to the

production of fine-grained images because the relatively low rate of development permits the sulfite to exert more solvent action which progresses with time."

Other studies of the Metol-hydroquinone-borax developer have been made.^{18,19}

Modern research techniques have been used to study the nature of the development given by the D-76 developer. The combination of low alkalinity and high sulfite concentration is responsible for the fine-grain characteristics of the solution. Reducing the sulfite also led to a loss in speed.⁷ G. I. P. Levenson⁸ has found that "Optimum emulsion speeds are obtained with a zero concentration of bromide." Thus, used D-76 may produce less film speed than the unused solution. Even modern research techniques have been unable to explain completely the unique properties of what is essentially a solution of Metol-free base in 10% sodium sulfite, the borax having been used to just neutralize the acidity of the Metol salt, and the hydroquinone being an ineffective developing agent at the pH of the solution.

Dissolve the chemicals in the order listed in Table 2. Filter the water to remove all foreign particles. Use distilled water, if possible. All water should be neutral (pH 7). If not, boil, then cool before mixing developer solutions.

Table 2. Developer Formulas

| Ingredient ^a | Kodak D-76 | Kodak D-76R ^b | Kodak D-76b | Kodak D-76d | Adox MQ | Anso 17 |
|---------------------------------|------------|--------------------------|-------------|-------------|----------|----------|
| Water (125°F or 52°C) | 750 ml | 750 ml | 750 ml | 750 ml | 750 ml | 750 ml |
| Metol | 2 | 3 | 2.75 | 2 | 2 | 1.5 |
| Sodium sulfite (anhydrous) | 100 | 100 | 100 | 100 | 80 | 80 |
| Hydroquinone | 5 | 7.5 | 2.75 | 5 | 4 | 3 |
| Borax | 2 | 20 | 2.5 | 8 | 4 | 3 |
| Boric acid | — | — | — | 8 | — | — |
| Potassium bromide | — | — | — | — | 0.5 | 0.5 |
| Water to make | 1 liter | 1 liter | 1 liter | 1 liter | 1 liter | 1 liter |
| Dev. times (min) (68°C or 20°C) | 9 to 17 | | | | 10 to 19 | 10 to 20 |

^a All ingredient quantities are in grams unless indicated otherwise.

^b Add 30 ml of D-76R solution for each 120 or 36-exposure, 35mm roll of film processed in the D-76 developer, discarding the used D-76 solution, if necessary, to maintain the original solution volume.